

Transient Shear Response of Liquid Crystal-Forming Hydroxypropyl Cellulose Solution in Dimethylacetamide.

II. Correlation Between Band Formation and Stress Relaxation

SHINICHI SUTO, * KENICHI KOHMOTO, and ATSUSHI ABE

Department of Polymer Chemistry, Faculty of Engineering, Yamagata University,
Jonan 4-3-16, Yonezawa, Yamagata 992, Japan

SYNOPSIS

The simultaneous determination of band formation and stress relaxation behavior was carried out using a parallel glass plates apparatus for the liquid crystalline hydroxypropyl cellulose solutions. The effects of shear rate and concentration on both behavior were mainly determined. The dependence of band formation on shear rate was the same as that reported in the literature: the higher shear rate is, the more rapidly the band forms. The band formation depended on the concentration. The effect of concentration appeared to depend on the solution phase (biphase or fully liquid crystalline phase); for the biphasic solutions, the band formed rapidly with increasing concentration, whereas for the fully liquid crystalline solutions, the band formed rapidly with decreasing concentration. Qualitatively, the stress relaxation was divided into two regions; one was the first rapid relaxation process, and another was the secondary slow relaxation one. It was speculated that the band does not form in the first process, but begins to form around the beginning of the secondary process. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The band formation behavior in the lyotropic and thermotropic liquid crystals (LCs) has been reported by many groups.¹⁻¹⁸ The band is known to form during the stress relaxation process, not during shearing. Interestingly, the band formation takes a time after cessation of shear. The time, t_b , depends on shear rate and shearing time.^{9-11,13-15} Furthermore, the band texture depended on other experimental and material conditions.^{5,10,12} Marrucci et al.¹⁰ reported the strong effect of sample thickness on the band formation, but Fincher¹² and Ernst et al.⁹ found little effect of sample thickness on the band spacing. Ernst et al.⁹ excluded the concentration dependence of the band formation based on the equation according to Doi and Edwards. However, Horio, et al.⁵ and Fincher¹² showed that the solution concentration is a very important parameter. The sys-

tematic study on the concentration dependence of the band formation was less. Then, we choose the concentration as the main parameter in this study. Furthermore, to understand fully the band formation behavior of LCs, we need to determine simultaneously the band formation behavior (optical observation) with rheological stress relaxation behavior. The simultaneous determinations are expected to provide some new informations regarding the band formation behavior.

In this study, we focus on the concentration dependence of the time t_b for the lyotropic LCs. The characteristic time t_b was determined by polarized microscopy, and simultaneously the stress relaxation behavior was determined by using a parallel plate apparatus designed and constructed by us at room temperature. Hydroxypropyl cellulose (HPC) solution in dimethylacetamide (DMAc) was mainly used. The effects of shear rate and polymer concentration on both t_b and stress relaxation behavior were determined and the band formation and stress relaxation behavior was compared.

* To whom correspondence should be addressed.

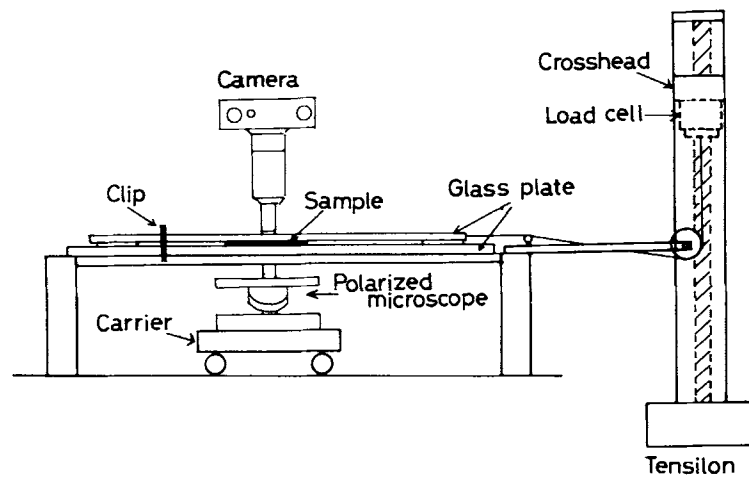
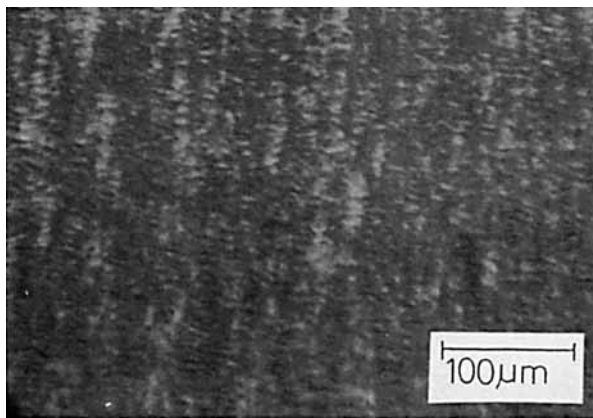
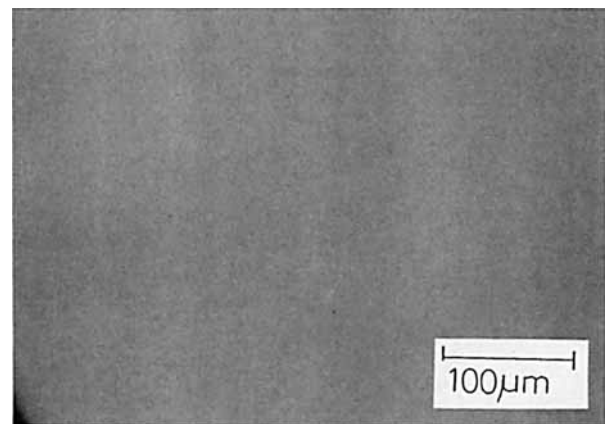


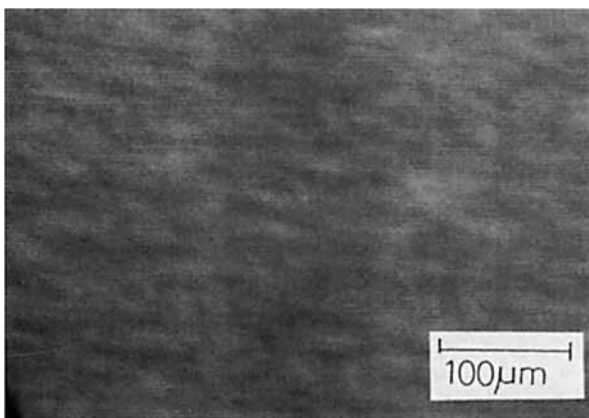
Figure 1 Schematic drawing of the parallel plates apparatus for observing band formation and stress relaxation behavior.



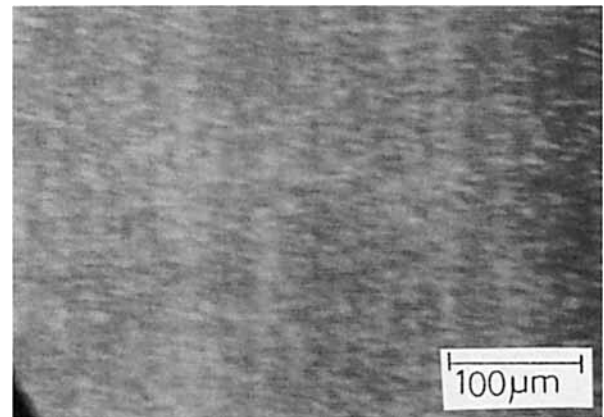
a)



b)



c)



d)

Figure 2 Polarized optical micrographs of the textures for 55 wt % HPC/DMAc solution: (a) at rest; (b) at shear rate of 53.8 s^{-1} ; (c) at t_b ; and (d) at t_s .

EXPERIMENTAL

Samples

HPC, DMAc and the concentrated solutions used in this study were the same as those in Part I of a two-part series.¹⁹ The characteristic concentrations Ca and Cb for the system at 25°C were 47 and 54 wt %, respectively.¹⁹ Commercial reagent grade

methanol and *m*-cresol (Wako Pure Chemical Co. Ltd.) were also used in this study. The liquid crystalline solutions (LCSs) in methanol were prepared by storing in a refrigerator at ca. 10°C for ca. 1 month, and the LCS in *m*-cresol was done by storing the refrigerator for ca. 3 months. The concentrations for the methanol system were 50, 55, 58, 60.2, and 64 wt %, and the concentration for the *m*-cresol system was 30 wt %.

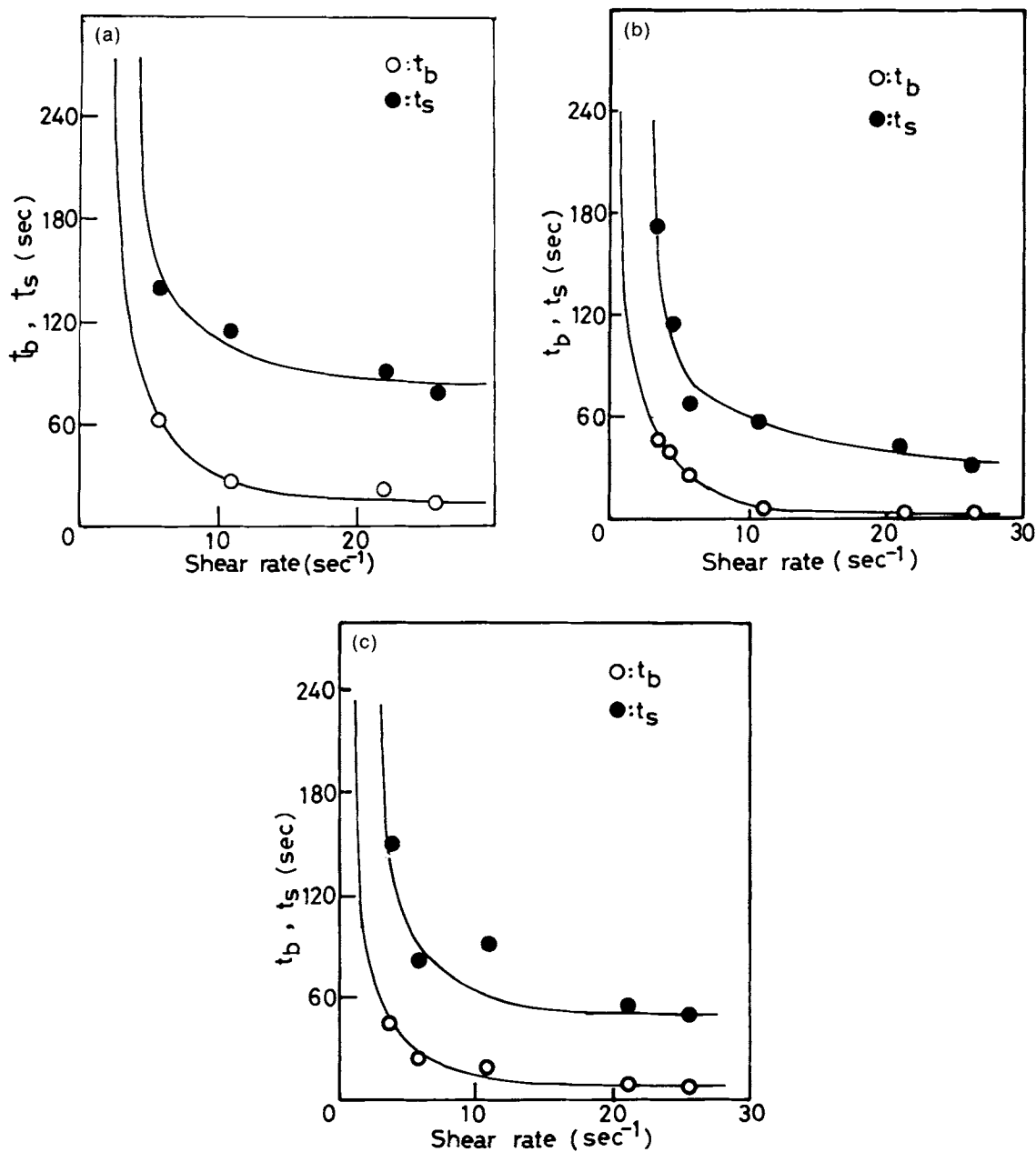


Figure 3 Dependence of characteristic times, t_b and t_s , on shear rate for liquid crystalline solutions: (a) 55 wt % HPC/DMAc; (b) 55 wt % HPC/methanol; and (c) 30 wt % HPC/*m*-cresol. Displacement length for each system is 5 cm.

Parallel Plate Apparatus

Figure 1 shows schematically our apparatus. The apparatus basically consisted of two parts: one part is parallel two glass plates (size: 600 mm long \times 20 mm wide) and another is Tensilon (UTM-III-500, Toyo Baldwin Co. Ltd.). Tensilon was used for sliding an upper glass plate at constant speeds; the lower plate was stationary. Between the plates, cover glasses with a given thickness (0.055 mm) were placed to control the sample thickness. In this study, the plate gap was held constant at 0.055 mm. The gap thickness and parallelism of the plates were measured by means of a travelling micrometer. With stainless wire, the upper plate was connected to a load cell (capacity: 5 kg) which was attached to the crosshead of Tensilon; the upper plate speed was changed by controlling the up-speed of the crosshead (2–500 mm/min). Texture of the LCSs was observed with an Olympus polarized microscope equipped a camera.

A given sample solution was spread to a length of 15 cm on the lower plate and was covered with the upper plate; after 30 min rest, the crosshead was moved up at a given speed and the load applied to the sample solution was recorded on a chart paper. The displacement length of upper plate was 3, 5, or 7 cm relative to the lower plate. Unless otherwise noted, the displacement length was 3 cm for the stress relaxation measurements. After stopping the crosshead, the change in texture was observed and the t_b was determined. After elapsing the time t_b , the band formed. The band, however, began to disappear gradually^{7,13} at a critical time which was abbreviated as t_s . (Note: the t_s is not the time when the band perfectly disappears, but the time when the band begins to disorder.) The time t_b could be determined with relative ease, but the time t_s with difficulty. Then, the reproducibility of t_s was not so good (better than 7%).

RESULTS AND DISCUSSION

Formation and Disappearance of Band

Figures 2 show a series of polarized microphotographs of typical band textures for the 55 wt % HPC/DMAc solution at a shear rate of 53.8 s^{-1} . The other solutions with different concentrations (over Ca) and with different solvent systems (methanol and *m*-cresol) exhibited the similar band formation and disappearance behavior. The band formation and disappearance behavior was greatly dependent on shear rate as Ernst et al.⁹ and Fried

et al.¹³ have reported. The shear rate dependence of the times t_b and t_s for the HPC/DMAc, HPC/methanol and HPC/*m*-cresol solutions is shown in Figure 3. Those characteristic times exponentially decreased with increasing shear rate. The dependence

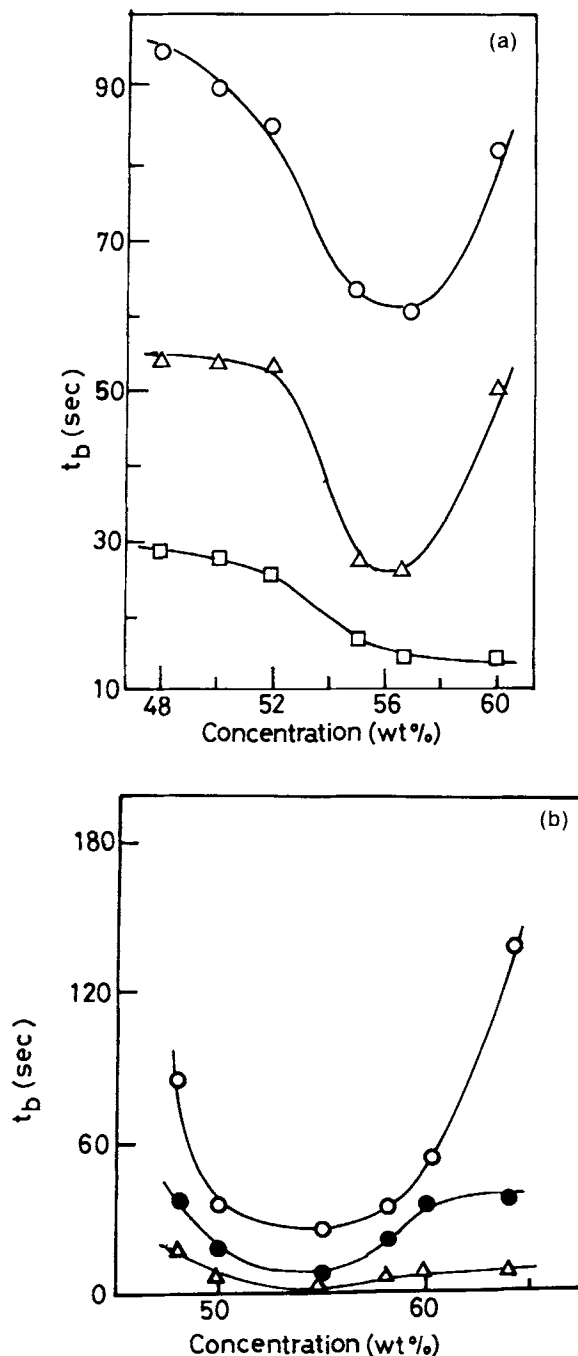


Figure 4 Dependence of characteristic time t_b on concentration: (a) HPC/DMAc solution; shear rate (s^{-1}): \circ 5.4, \triangle 10.8, and \square 26.9; (b) HPC/methanol solution; shear rate (sec^{-1}): \circ 5.4, \bullet 10.8, and \triangle 21.5.

of t_b on shear rate was the same as those for the HPC LC systems^{9-11,13-15} and other LC systems.^{15,20} There was a critical shear rate above which the band forms. The critical shear rate was almost independent of concentration as Ernst et al.⁹ have reported. The dependence of t_s on shear rate was almost the same as that of t_b . The gap between t_s and t_b , the duration time for which the band keeps a steady form, tended to decrease and to become constant with increasing shear rate. This trend was the same as that by Ernst et al.⁹ The reincrease in t_b at higher shear rates¹⁵ was not observed within experimental range.

Figure 4 shows the dependence of t_b on concentration for the HPC/DMAc and HPC/methanol systems at each shear rate. The time t_b exhibited a minimum with respect to concentration. The concentration at minimum was around 55 wt % for both systems. However, the behavior exhibiting a minimum became less remarkable with increasing shear rate and the time t_b decreased monotonously with increasing concentration at a shear rate of 26.9 s^{-1} . Another feature in Figure 4 was that the biphasic solutions (between 47 and 54 wt %) also exhibits the band behavior. Ernst et al.⁹ reported that the HPC biphasic solutions in water form no band.

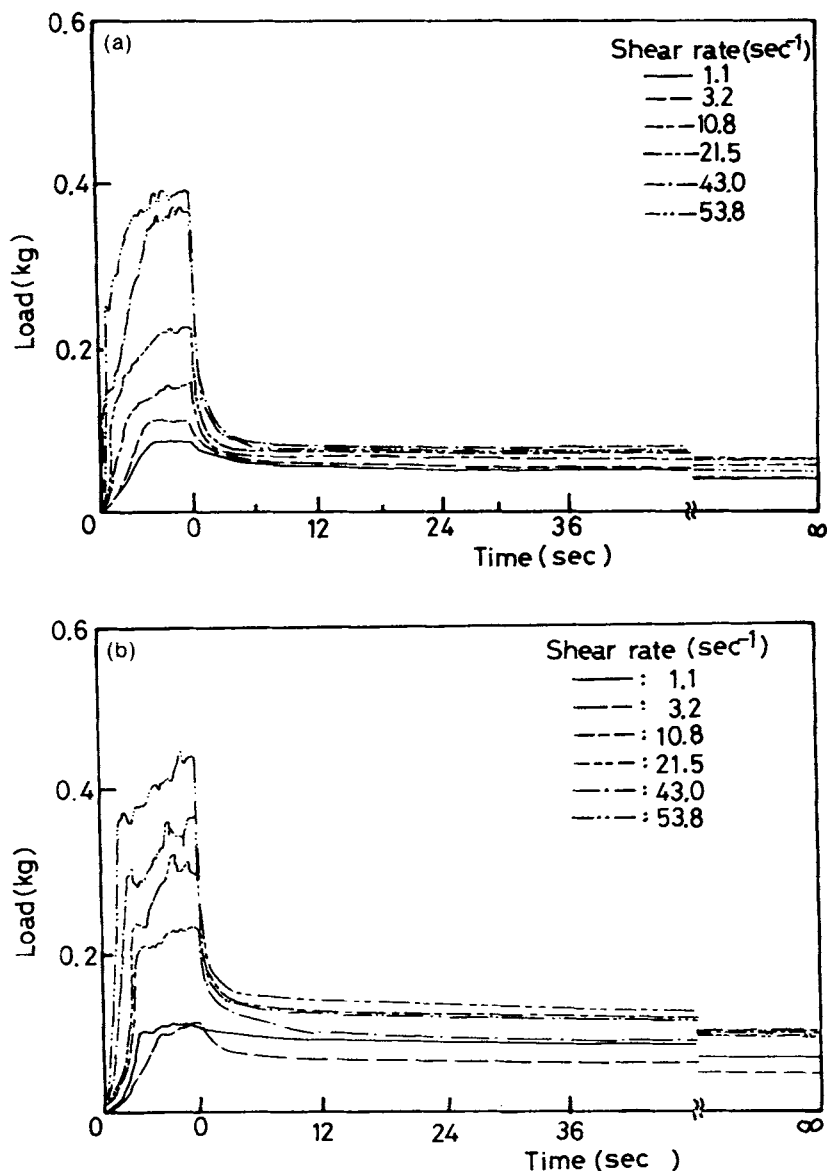


Figure 5 Stress growth and relaxation curves at each shear rate for HPC/DMAc solutions. The displacement length is 3 cm. Concentration (wt %): (a) 31.8; (b) 60.

Stress Relaxation Behavior

Figure 5 show the stress growth and relaxation behavior at given shear rates for the HPC/DMAc system. The isotropic solution (31.8 wt %) exhibited a normal behavior; the stress increased with increasing time and finally reached a plateau, that is, steady state. On the other hand, LCS (60 wt %) exhibited a stress overshoot. For the LCS, it was not clear whether the stress on growth process becomes steady state or not, especially at higher shear rates. Therefore, we determined the stress growth behavior by changing the displacement length. Figure 6 shows the effect of displacement length on the stress growth for the 60 wt % solution at a shear rate of 53.8 s^{-1} . The stress around the plateau for the 3-cm displacement was almost the same as that for the 7-cm displacement. This showed that the 3-cm displacement is enough to attain a steady state at each shear rate within our experimental range. It was noteworthy that the relaxation behavior depends on the displacement length: the longer the displacement is, the more rapidly the stress relaxes; the displacement effect corresponded to the effect of shearing time or shear strain. It is needless to say that the t_b decreases with increasing displacement length.

In Part I of this two-part series,¹⁹ we proposed an analytical method for the stress relaxation of the LCSs. Following the method, we normalized the stress during relaxation process in Figure 5. The plots of normalized stress versus time are shown in

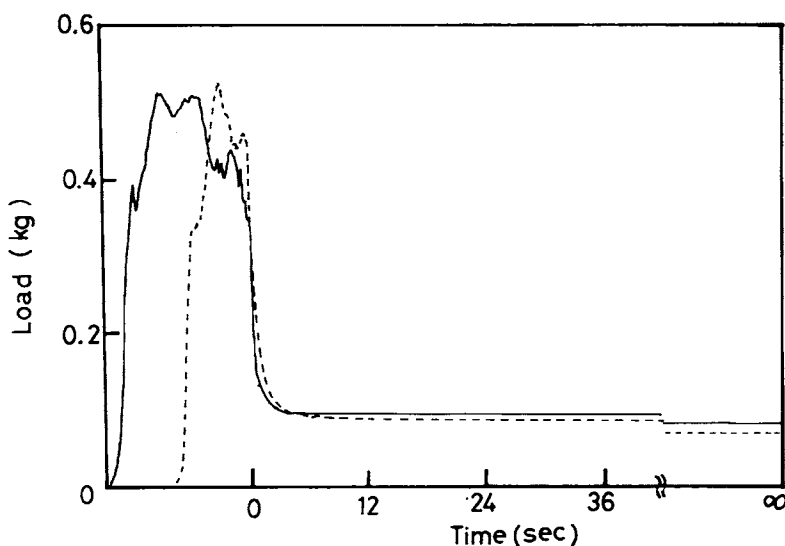


Figure 6 Effect of displacement length on stress growth behavior for 60 wt % HPC/DMAc solution at shear rate of 53.8 s^{-1} . Displacement length (cm): (----) 3; (—) 7.

Figure 7. We expected that such a plot as shown in Figure 7 exhibits one straight line for the isotropic solutions and two straight lines for the LCSs.^{19,21} Clearly, the curves at given shear rates were non-linear, regardless of concentration. Consequently, no relaxation times for each solution could be evaluated. This was partially because the solution in the parallel apparatus was subjected heterogeneously to shear and the shear rate distribution in the solution was nonuniform. An assumption of a simple shear flow between parallel plates was not valid in our case. Therefore, the shear rates shown in our figures were apparent ones. However, it was found qualitatively that the relaxation curves consist essentially of two regions; the first rapid decrease region and the secondary slow decrease region. The first region depended on shear rate: the higher the shear rate is, the greater the decrease in stress is. On the basis of our findings,^{19,21} this suggested that the relaxation time in the first region depends on shear rate and decreases with increasing shear rate. The decrease in relaxation time with increasing shear rate for our system was the same trend as that for the ethyl cellulose/*m*-cresol system²¹ and for the suspension system.²²

Comparison with band formation and stress relaxation behavior

Figure 8 shows the relaxation curves for the 60 wt % HPC/DMAc solution as Figure 7. The band for-

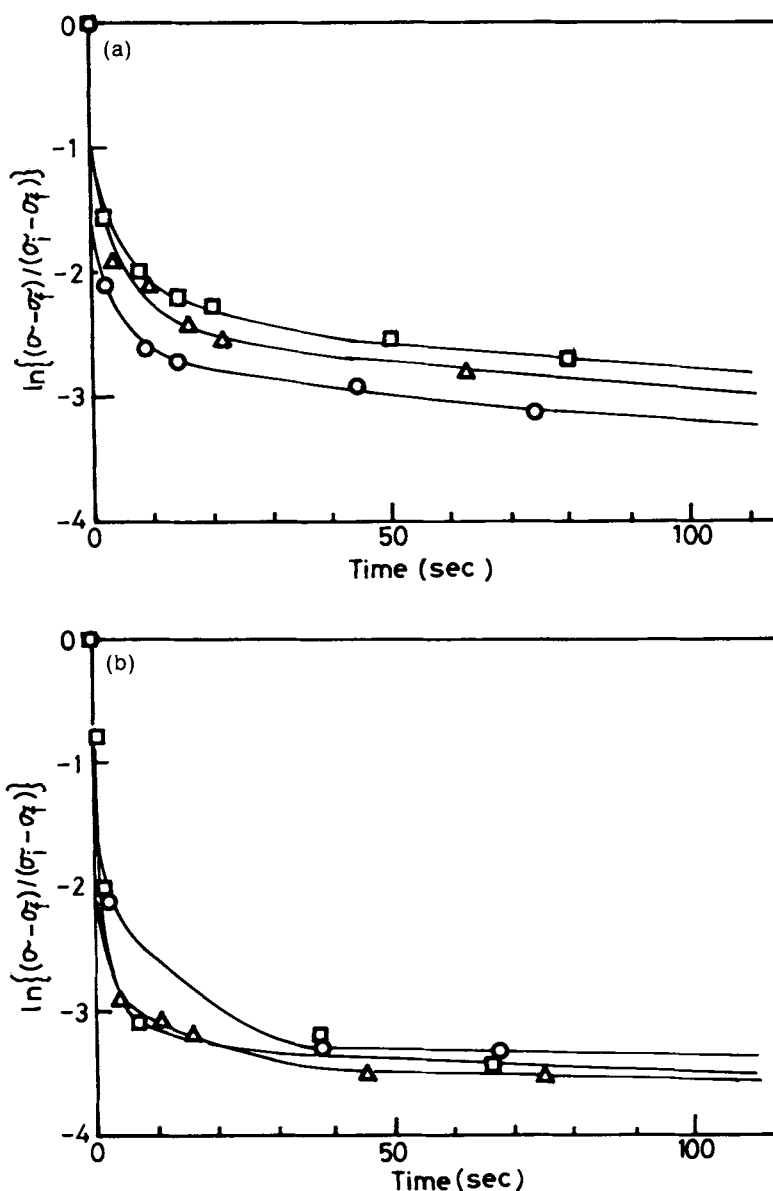


Figure 7 Normalized stress relaxation curves for HPC/DMAc solutions after cessation of shear flow at 43 s^{-1} . Displacement length (cm): \circ 7, \triangle 5, and \square 3. Concentration (wt %): (a) 50; and (b) 60.

mation data are represented together; the wide line for each curve indicates the gap between t_b and t_s . The t_b and t_s are the extreme right and left of each wide line, respectively. The data in Figure 8 showed that the band begins to form around the end of the first rapid relaxation region. Figure 9 shows the similar curves for the 55 wt % HPC/DMAc solution. The data in Figure 9 confirmed that the band formation is related to the beginning of the secondary slow relaxation region. In Part I of two-part series,¹⁹

we described that the HPC LCSs in DMAc have two relaxation mechanisms and the rapid relaxation mechanism transfers into another slow relaxation mechanism at the characteristic time t_c . Therefore, the t_c is expected to have some correlation to the time t_b at which the band begin to form. Figure 10 shows the relation between t_b and t_c for the HPC/DMAc system. The parameter is the concentration (48, 50, 52, 55, 57, and 60 wt %). Figure 10 gave a relatively good correlation for two characteristic

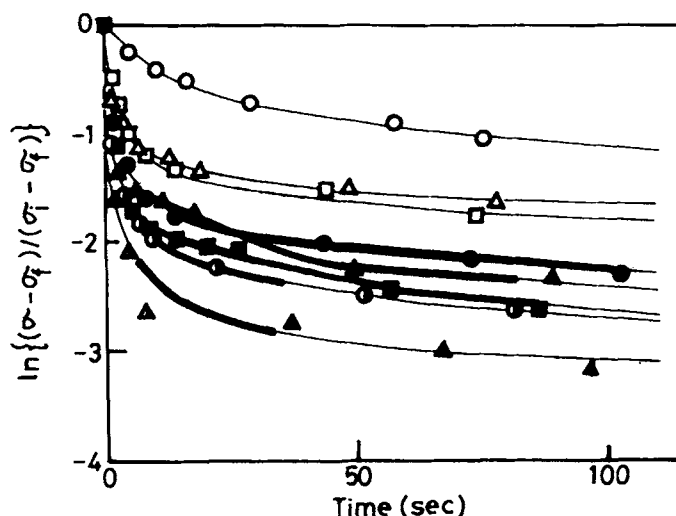


Figure 8 Simultaneous representation of band formation and stress relaxation behavior for 60 wt % HPC/DMAc solution. Shear rate (s^{-1}): \circ 1.1, \triangle 3.2, \square 5.4, \bullet 10.8, \blacktriangle 21.5, \blacksquare 32.3, \blacklozenge 43, and \blacktriangledown 53.8.

times, taking into account the difficulties that the determination of t_b must encounter. This implies that no band forms during the first rapid relaxation process (A_1 process in Part I¹⁹), and the band begins to form after the relaxation mechanism transfers into the secondary process (A_2 process). To conclude explicitly our findings noted above, we need the data of t_c determined by means of parallel plates apparatus.

Figure 11 shows the relation between the t_b and the relaxation times and steady-state shear viscosity

determined in our previous paper,¹⁹ with respect to concentration. Each parameter exhibited a minimum. This suggested that the band formation depends on the solution phase. For the biphasic solution (mixture of isotropic and LC phases), less than 55 wt %, the t_b tended to decrease with increasing concentration, and on the contrary, the t_b tended to increase for the fully LC phase (greater than 55 wt %). Putnam et al.¹⁶ reported that the relaxation at higher concentration was more rapid than that at lower concentration for the HPC/water system,

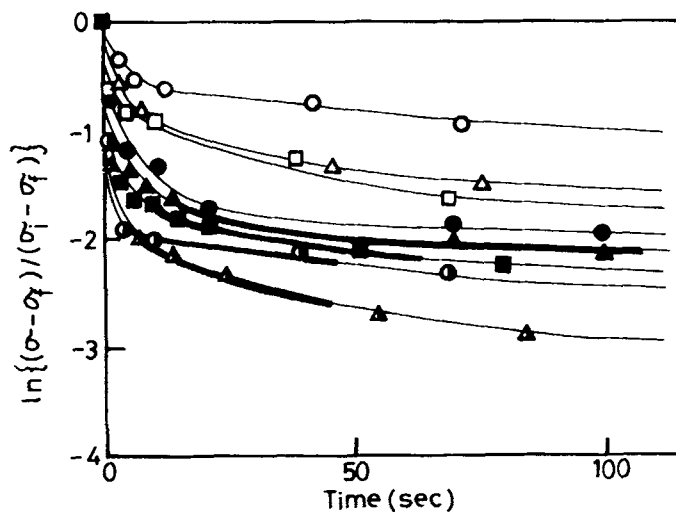


Figure 9 Simultaneous representation of band formation and stress relaxation behavior for 55 wt % HPC/DMAc solution. Shear rates are the same as in Figure 8.

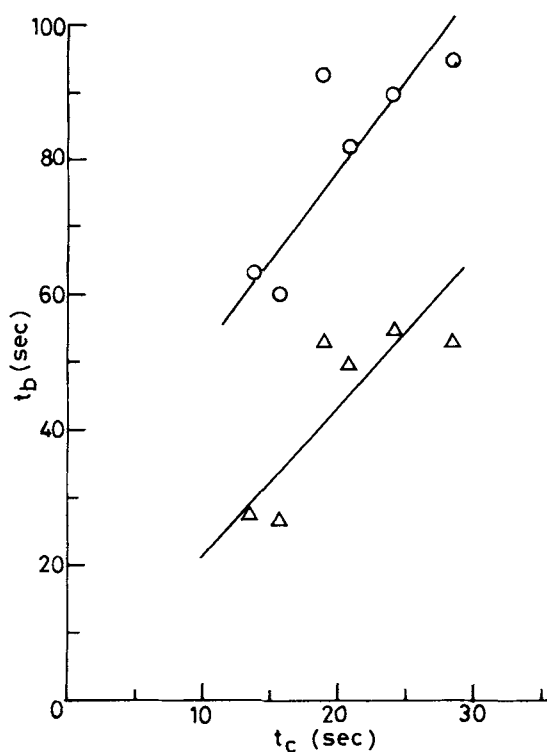


Figure 10 Correlation between characteristic times, t_b and t_c , for HPC/DMAc solution. For t_b , shear rate (s^{-1}): ○ 5.4, △ 10.8. t_c is the characteristic time where the rapid relaxation process transfers to the subsequent process.¹⁹ Concentrations are 48, 50, 52, 55, 57, and 60 wt %.

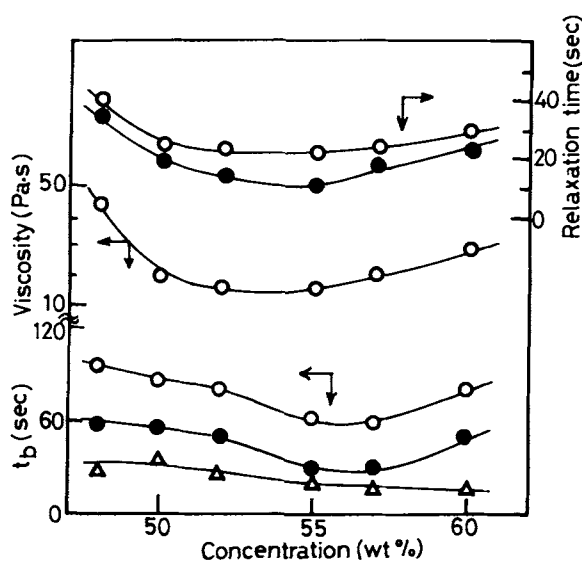


Figure 11 Concentration dependence of t_b , shear viscosity at shear rate of $1 s^{-1}$, and relaxation times for HPC/DMAc solutions. For t_b , shear rate (s^{-1}): ○ 5.4, ● 10.8, and △ 21.5. For relaxation times, τ_1 (●) and τ_2 (○), see Ref. 19.

Table I Summary of Dependences of Parameters on Concentration and Shear Rate

	t_b	t_c	τ_1	τ_2	η
Concentration	Biphase	↘	↘	↘	↘
	Fully LC phase	↗	↗	↗	↗
Shear rate	↘		↘	↘	↘

but the opposite trend is observed for the HPC/methanol system. Their data for the HPC/water system were inconsistent with our data on relaxation time. As Charlet et al.^{23,24} described, the HPC/water system had a width of biphasic range and the width greatly depended on temperature. We presume that the data for the HPC/water system by Putnam et al.¹⁶ were possibly in different phase; in their paper, no data for measurement temperature was given. Marsano et al.¹⁵ have pointed out the role of the steady-state viscosity in the band formation; the dependence of the t_b on shear rate showed a critical shear rate at which the reincrease of t_b appears, and at the shear rates less than the critical shear rate, the t_b decreased with increasing viscosity, and at the shear rates greater than the critical shear rate, the t_b increased by larger viscosity. Our data shown in Figure 11 were consistent with the case at the higher shear rate reported by Marsano et al.¹⁵ However, our data were determined at relatively low shear rates and seemed unlikely to be greater than the critical shear rate. When we consider the role of viscosity in the band formation, we need to know whether the change in viscosity exhibits in the same phase (biphase or fully LC phase), or in the different phase (biphase and fully LC phase). Because the dependence of t_b on the viscosity in the biphase was different from that in the fully LC phase; the reverse dependence on the viscosity was found in our study. The dependence of each parameter on concentration and shear rate is summarized in Table I. Consequently, as noted above, we suggest that the solution phase (biphase or fully LC phase) plays an important role in the band formation, especially in the t_b .

CONCLUSIONS

The t_b depended on the concentration and exhibited a minimum around 55 wt % (ca. Cb). The stress relaxation times could not be evaluated using our

parallel apparatus, but qualitatively the relaxation curves were divided into two regions: one was a relatively rapid relaxation process, and another was a slow relaxation process. It was speculated by comparison with the band formation and stress relaxation behavior that the band begins to form at the characteristic time when the rapid relaxation mechanism transfers into the slow relaxation mechanism. The band formation appeared to depend on the solution phase (biphase or fully LC phase); the concentration effect was contrary.

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